OCT 9 1923

59—2

Proceedings of the American Academy of Arts and Sciences.

Vol. 59. No. 2.— September, 1923.

(CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. MEMORIAL LABORATORY OF HARVARD UNIVERSITY.)

A REVISION OF THE ATOMIC WEIGHT OF BORON.

THE ANALYSIS OF BORON TRICHLORIDE AND BORON TRIBROMIDE.

By Gregory Paul Baxter and Arthur Ferdinand Scott.

(Continued from page 3 of cover.)

VOLUME 59.

1. DURAND, ELIAS J.— The Genera Midotis, Ionomidotis and Cordierites. pp. 1–18. 2 pls. September, 1923. $.80.
2. BAXTER, GREGORY PAUL AND SCOTT, ARTHUR FERDINAND.— A Revision of the Atomic Weight of Boron. The Analysis of Boron Trichloride and Boron Tribromide. pp. 19–48. September, 1923. $.80.

Proceedings of the American Academy of Arts and Sciences.

Vol. 59. No. 2.— September, 1923.

(CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. MEMORIAL LABORATORY OF HARVARD UNIVERSITY.)

A REVISION OF THE ATOMIC WEIGHT OF BORON.

THE ANALYSIS OF BORON TRICHLORIDE AND BORON TRIBROMIDE.

By Gregory Paul Baxter and Arthur Ferdinand Scott.

(CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE JR. MEMORIAL LABORATORY OF HARVARD UNIVERSITY.)

A REVISION OF THE ATOMIC WEIGHT OF BORON.

THE ANALYSIS OF BORON TRICHLORIDE AND BORON TRIBROMIDE.

By Gregory Paul Baxter and Arthur Ferdinand Scott.

Received May 27, 1923. Presented May 9, 1923.

CONTENTS.

Introduction 21
Purification of Materials 22
Preparation of Boron Trichloride 25
Preparation of Boron Tribromide 31
Analysis of Boron Trichloride 33
Analysis of Boron Tribromide 37
Results 39
Discussion of Results 42
Summary 47

Introduction.

During recent years until 1918 the value 11.0 for the atomic weight of boron was in common use.[1] In that year, however, Smith and Van Haagen [2] published the results of a strikingly consistent series of experiments in which weighed quantities of anhydrous borax were converted into sodium chloride, sulfate, fluoride, nitrate and carbonate, either directly or with the intervention of acetic acid. While the number of experiments of each sort was in general small, the remarkable concordance in the values for the atomic weight of boron obtained from the varied ratios fills the reader with admiration for the extraordinarily accurate analytical technique of the experiments, and leaves no question but that in this respect nothing more could be desired. The value for the atomic weight of boron was found to be 10.900, a value subsequently adopted by the International Committee on Atomic Weights. One of the chief obstacles encountered by Smith and Van Haagen was found to be the complete dehydration of borax, and they impute to this difficulty the divergence from theirs of most of the earlier values based on the analysis of borax.

Only one sample of borax was prepared by Smith and Van Haagen,

by neutralizing recrystallized sodium carbonate with a slight excess of boric acid. Although this specimen was crystallized, fused and recrystallized before the final dehydration, the question may well be raised as to whether its composition could be represented exactly by the conventional formula. Smith and Van Haagen state:

"Reliable tests indicating the presence, in borax, of traces of other borates (either more basic or more acid in character) are lacking. However, such borates are prepared only with difficulty and as, in the present instance, the proportion of the components and the conditions of formation were those corresponding to the tetraborate with ten molecules of water, it may safely be assumed that the preparation was pure also from this point of view."

It is nevertheless true that borates in which the ratio of sodium to boron varies from 1 to 1, even to 1 to 5 have been prepared.[3] Therefore it is conceivable, owing to the complicated nature of borax solutions and to the presence of the slight excess of boric acid used by Smith and Van Haagen in the preparation of their borax, that their material occluded small amounts of salts more acid than borax. The effect of such occlusion would be to raise the apparent atomic weight of boron.

In view of this possibility it is unfortunate that specimens of borax crystallized initially from solutions of somewhat different composition were not compared, in order to make certain that the composition of the recrystallized salt is really independent of small variations in the conditions of preparation.

Because of the low atomic number and isotopic character of boron, its atomic weight is a particularly interesting one. Therefore in order to obtain further evidence in the matter we have purified and analyzed both the trichloride and the tribromide. In a brief note the preliminary result of these analyses has already been stated[4] to be 10.83 ± 0.01. The final result, 10.82, agrees exactly with the result of the analysis of boron trichloride recently published by Hönigschmid and Birckenbach.[5] Still more recently, in a preliminary communication, Stock and Kuss,[6] by measuring the hydrogen evolved in the decomposition of diboran with water, have obtained the value 10.81.

Purification of Materials.

Water.— Ordinary distilled water was twice redistilled, once from alkaline permanganate and once from very dilute sulfuric acid. The condensers were block tin tubes, fitted to Pyrex flasks with constricted necks, which served as stills. The connection was made by

a water seal, no cork or rubber being used. The water was collected in Jena flasks, generally just previous to use.

Nitric Acid.— Concentrated C. P. nitric acid was distilled through a quartz condenser, the first two-thirds as well as the last tenth being rejected.

Bromine.— This material was purified according to the method which has been frequently used at Harvard.[7] Crude bromine was first distilled from aqueous potassium bromide in order to remove chlorine. Next one-fourth of the product was converted to potassium bromide by means of recrystallized potassium oxalate, and the remaining three-fourths of the bromine was distilled from solution in this potassium bromide. All the product was then converted to potassium bromide by means of potassium oxalate, and the potassium bromide was fused in a platinum dish with enough recrystallized potassium permanganate to oxidize all organic matter. In order to obtain bromine the purified potassium bromide was dissolved in a solution of pure sulfuric acid. The excess of potassium permanganate contained by the salt caused a small quantity of bromine to be liberated, which was removed by distillation since it might have contained a trace of iodine. Enough pure permanganate to liberate the greater portion of the bromine was then added, and the bromine was distilled into a receiver cooled with ice. In this last step the bromine received a third distillation from a bromide. The product was separated from the water, dried with resublimed phosphorus pentoxide and once redistilled. Small portions of similar bromine were furnished by Dr. P. F. Weatherill and Mr. M. J. Dorcas.

Silver.— This substance was prepared by standard methods. These consisted in brief of the following processes: double precipitation as chloride, followed by reduction with alkaline sugar solution, fusion of the metal on charcoal, solution and reprecipitation with ammonium formate, fusion on pure lime, electrolytic transport, fusion on pure lime in hydrogen, etching, drying in a vacuum at 500°C. Recent work by Baxter and Parsons [8] and Baxter [9] as well as earlier work have shown that these processes yield a product of adequate purity. Four other samples of silver which had been prepared in essentially the same way by Dr. Weatherill,[10] and Messrs. Tani,[11] Dorcas and Hilton,[12] were used in certain analyses as indicated later.

Chlorine.— This substance was drawn directly from a large tank of liquid material, a considerable portion of which had already been used. It was purified and dried by passing through two towers filled with beads wet with water, then three similar towers containing concentrated sulfuric acid, and finally through a tube containing resub-

limed phosphorus pentoxide. The purifying apparatus contained no rubber except one very short connection with the tank.

Helium.— This gas was very kindly provided by the United States Navy Department. In order to remove the greater part of the nitrogen and hydrocarbons the helium, after passing through a gas washing bottle containing concentrated sulfuric acid, was conducted through a hot hard glass tube containing metallic calcium to remove nitrogen, and copper oxide to oxidize hydrogen and hydrocarbons. The product then passed over aqueous silver nitrate, concentrated aqueous sodium hydroxide, concentrated sulfuric acid and resublimed phosphorus pentoxide in sequence. Rubber connections were avoided beyond the hard glass tube.

Boron.— Since the halides were prepared by synthesis from the elements, it was necessary to prepare elementary boron. This was done by the reduction process of Moissan,[13] which consists in combining magnesium with boron trioxide and extracting the product with acid. In one preparation an excess of boric oxide was used, so that the so-called boron suboxide resulted. This material proved unsatisfactory from the standpoint of reactivity with halogens, so that nearly all our material was prepared with an excess of magnesium. The greater portion of this excess was ultimately extracted with acid, but residual magnesium or magnesium boride could do no harm owing to the low volatility of magnesium halides.

To prepare the suboxide the trioxide was mixed with powdered magnesium in the proportions of 3 to 1, and the mixture, contained in a sand crucible, was placed in a muffle which already had been heated to dull redness with a blast flame. At this temperature the reaction soon started and progressed rapidly throughout the mass. After cooling, the contents of the crucible were extracted with an excess of hydrobromic acid and the residue was washed by decantation until the washings were neutral. Centrifugal settling in glass receptacles materially hastened the progress of the washing. The product was first dried in an oven, and finally at 200° in a vacuum. This material was originally intended for the preparation of boron tribromide and on this account was extracted with hydrobromic acid. It was actually used in preparing the first specimen of the trichloride.

For all the other work boron was made from a mixture of the trioxide with magnesium in the proportions of 1 to 1.5 by a process similar to that outlined above. The bulk of the magnesia resulting from the reaction together with a large part of the excess of magnesium was first extracted with acid and the residue washed. Then the boron was twice boiled for some time with concentrated acid with inter-

mediate washing. After a final thorough washing with water the material was dried in the air at 110° to 120° for some time, and then at 200° in a high vacuum. Since in spite of the careful extraction the material was found to retain halide, for preparing the trichloride and tribromide separate specimens were made in exactly the same way, except that each was extracted with the appropriate acid.

The Preparation of Boron Trichloride.

Two specimens of boron trichloride were prepared. The first was made by heating boron suboxide in a current of dry chlorine. The suboxide was contained in a hard glass tube connected by ground glass joints at one end to the chlorine purifying train (see page 23), at the other to two receiving bulbs also connected by a ground glass joint. The hard glass tube was electrically heated to dull redness. The first receiving bulb was cooled with ice, the second with alcohol-carbon dioxide mixture. At first the chlorine was almost completely used up, but after several hours operation the gases produced showed by their color that they contained much uncombined chlorine. The process was therefore stopped at this point. After a second similar preparation had been made, the two portions of trichloride were combined in one bulb, and, after the addition of mercury, the bulb was exhausted by means of an efficient water pump through a capillary tube and sealed. Owing to the relatively high vapor pressure of boron trichloride the greater part of the air contained by the bulb was swept out by the tri-chloride vapor during the exhaustion. At the same time the low boiling impurities such as hydrogen chloride were partially eliminated.

At this point the trichloride was known or suspected to contain the following impurities: free chlorine, the products of hydrolysis owing to unavoidable slight exposure to moist air, i.e., boric acid and hydrogen chloride, boron tribromide from impurity in the boron which had been extracted with hydrobromic acid, and silicon tetrachloride. Wöhler and Deville [14] noted the contamination of boron trichloride with silicon tetrachloride in the case of material prepared in glass. As suggested by Stock and Priess,[15] who prepared the trichloride in a similar fashion, this difficulty may have resulted from impurity of silicon in the boron which was made in sand crucibles or from reaction of the boron and chlorine together on the hard glass tube. It was unlikely though possible that a small amount of carbon tetrachloride was present. Stock and Priess [15] and Stock and Kuss [16] found that the boron trihalides do not add halogen, and Stock, Kuss and Priess [17]

found that boron hydrides are converted to trihalide by an excess of halogen so that higher halides and substituted hydrides were not to be feared.

The free chlorine was readily removed by shaking with mercury in the first bulb. The original yellow color of the liquid nearly disappeared and the liquid after distillation into a second bulb, also containing mercury, scarcely tarnished the latter substance. The remaining substances were eliminated by fractional distillation in vacuum. From the following table it can be seen that the boiling points of all the impurities are so far removed from that of boron trichloride that, unless constant boiling mixtures with boron trichloride exist, sufficiently complete separation could be hoped for.

	Bpt.
BCl_3	12.5°
BBr_3	90.5°
HCl	−83.1°
CCl_4	76.7°
$SiCl_4$	58.0°

The apparatus employed in the early stages of the fractionation is illustrated by Figure 1. The original bulb *A* containing the trichlo-

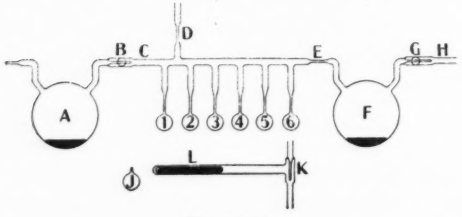

FIGURE 1.

ride was provided at the outset with a special joint *B*, by means of which it could be connected with apparatus sealed to it at *C*. The system terminates in a second large bulb *F* also attached to a special joint *G*. The special joint is shown on a large scale in the figure. The sealed-in capillary *K* is closed at the end and is scratched with a file at several points to facilitate breaking. To break the joint the closed tube of glass weighted with mercury *L* is allowed to strike the capillary with some force. This device was apparently first used by Bruner and Bekier [18] and has recently been employed in several investigations.[19] After the system to the right of *B* has been exhausted

with an efficient Gaede mercury pump and sealed at D, the joint at B is opened by breaking the capillary. The more volatile fractions of material are condensed in some of the small bulbs, 1, 2, 3, by means of liquid air or carbon dioxide-alcohol mixture and are sealed off as soon as filled. Then the main portion of material is distilled into F, which is sealed off at E, leaving the least volatile fraction in A. Subsequently, if desired, the residue in A can be distilled into 4, 5 and 6 for examination. A new system can now be sealed to F at H and the process repeated.

In this way the boron trichloride was distilled twenty times. In

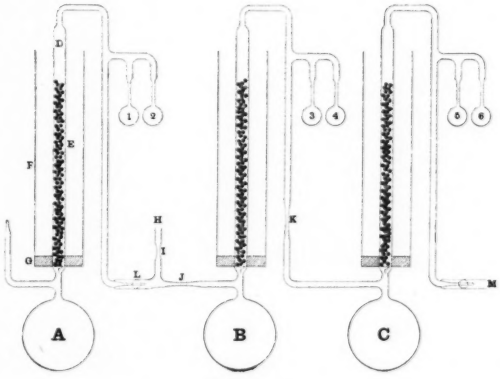

FIGURE 2.

the early distillations several small, more volatile fractions were rejected as well as several small, less volatile fractions. Later, since the silicon tetrachloride was removed rather slowly, none of the more volatile material was rejected, and the less volatile residue was collected as a single fraction. After the twentieth distillation we found that in spite of the low boiling point of the trichloride, a Hempel column could be employed without difficulty. Figure 2 shows the arrangement of a system for this purpose. The trichloride is at room temperature in bulb A. The Hempel column E filled with large glass pearls is cooled by filling the jacket F with alcohol-carbon dioxide until refluxing is apparent in the column. A temperature of $-15°$ to $-20°$ was found satisfactory. By chilling the bulb 1 to a still lower temperature a light fraction may be condensed, and after the joint L has been opened the main distillation into B may be carried

out. The bulb A is then disconnected by sealing J and the residue in A is condensed in the small bulb 2. With suitable adjustment of temperatures in similar apparatus many substances have recently been successfully and very efficiently fractionated in this laboratory.

The complete fractionation of Sample I of boron trichloride is indicated in Figure 3, in which each large circle represents a distillation. More volatile fractions removed are shown as small circles to the right, less volatile fractions to the left. These fractions were usually condensed in small bulbs, but sometimes merely were left in

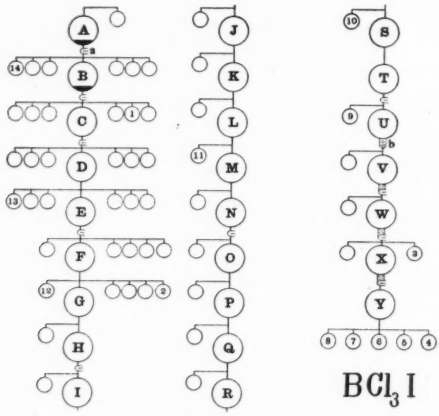

FIGURE 3.

the distilling flask. The special sealed-in joints are indicated as at a, Hempel columns as at b.

The least volatile fraction from the second distillation, 14, was decomposed with water in a platinum dish and the silica content was found to be 0.07 gram. Fraction 13 in a similar way yielded 0.10 gram, but since this fraction was much larger than 14, the result really indicates a smaller proportion. Repeated fractionation slowly increased the purity of the trichloride so that Fraction 10, about 3 gm., yielded only 2.0 mg. of silica. At this point the use of a Hempel fractionating column was begun. Fraction 9, weighing approximately 2.5 gram was found to yield 0.6 mg. silica. This proportion would raise the apparent atomic weight of boron 0.007 unit. After three more distillations with Hempel columns, the remaining material was collected in five fractions for analysis (Fractions 4 to 8).

The second sample of boron trichloride, as stated before, was made from boron which had been completely reduced with magnesium and extracted with hydrochloric acid. Otherwise its preparation did not differ from that of the first sample except that it was secured in a single operation. The bulb *A* (Figure 4), containing the trichloride and mercury, was cooled and exhausted by means of an efficient water aspirator. After the trichloride had been allowed to boil gently for a short time the system was sealed. In order to remove the free chlorine by combination with the mercury the bulb was fre-

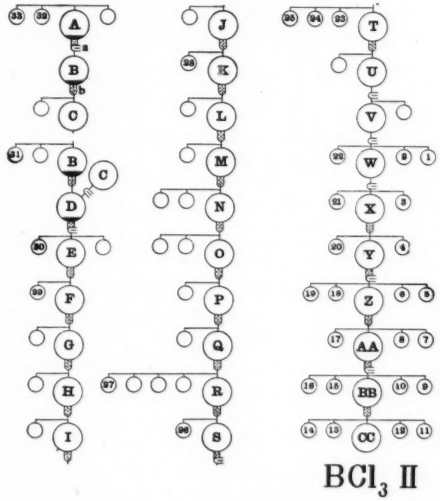

FIGURE 4.

quently shaken for a week. Since the yellow color still persisted, the material was distilled through a fractionating column into another bulb *B*, also containing mercury, with which it was left in contact for some time. Upon distillation into *C*, it was apparent that the chlorine had not been completely removed. Therefore a large part of the material was distilled back again into *B*, leaving a colorless liquid in *C*. The bulb *C* was then sealed off. After some time the material in both *B* and *C* was distilled into *D* also containing mercury. Prolonged agitation with mercury in *D* finally removed all trace of color.

In order to avoid the necessity of continually attaching and ex-

hausting new distilling apparatus, a system was constructed in which the same fractionating columns could be repeatedly employed.[15] The construction of this apparatus is shown in Figure 5. After sealing to the bulb *A* containing the trichloride, the system was exhausted and sealed off at *N*. By chilling *B* with carbon dioxide-alcohol mixture and suitable cooling of the column *E* the trichloride, was distilled into *B* and bulb *A* was sealed off at *P*. With *B* at room temperature, 13

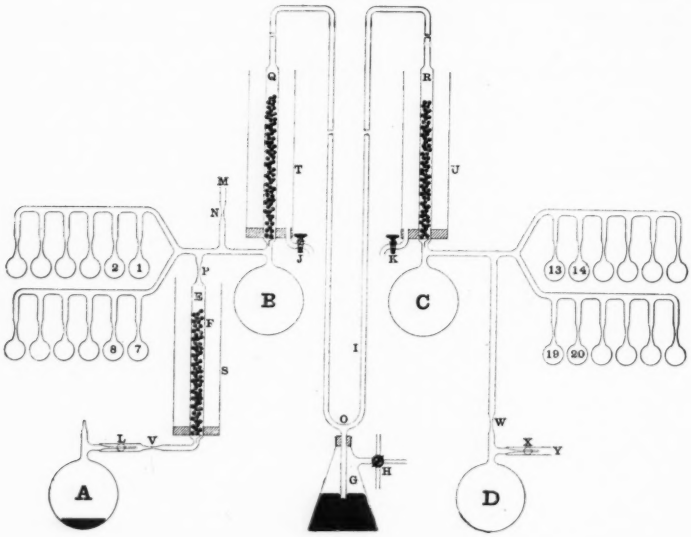

FIGURE 5.

was next chilled and a small fraction was removed through the column *Q*. The greater portion of the remainder was distilled into *C*, and when the residue in *B* was small, connection between *B* and *C* was closed by forcing pure mercury from *G* into the U-tube *O*. This mercury valve is a modification of one used by Stock and Priess.[15] The residue in *B* was finally collected in the bulb 1 while *B* and *Q* were both surrounded with hot water. The process was then repeated, *C* serving as still and *R* as the fractionating column. No volatile fraction was rejected but the least volatile was collected in 14. In all, thirteen such distillations were made and the remaining material was collected in *D* (Figure 5).

In Figure 4 the fractionation with the above apparatus includes the steps *E* to *S*. From *S* the distillation was continued by the earlier method. Since a crack in the fractionating column of *S* was suspected to have admitted a small amount of air, after distilling from *U* to *V*, a portion was distilled back to *U* which was immediately sealed off. In this way permanent gases were effectually flushed out. After distillation into *W*, the material was set aside for nine months. No change in appearance could be detected during this time. Eventually the distillation was continued until all the material had been collected in fractions.

In Figure 4 the fractions ultimately examined are numbered in the order of decreasing volatility, i.e., Fraction 1 is the most volatile of these.

Fractions 30 and 29 were found to contain considerable silicon tetrachloride, but since the proportion in 28 was much smaller than in 29, no other direct tests for silicon were made.

The Preparation of Boron Tribromide.

The boron tribromide was synthesized from the elements by saturating an inert gas with pure bromine and passing the mixture over boron which had been extracted with hydrobromic acid (see page 24). Since nitrogen reacts readily with boron at elevated temperatures, the gas used as a carrier for the bromine was helium. The purification of this gas is described on page 24. After passing through the purifying train the helium was bubbled through bromine in a glass bulb connected by a ground joint with the hard glass reaction tube containing the boron. This tube, as in the preparation of the trichloride, was connected by a second ground joint with two condensing bulbs the second of which was cooled in an ice bath, since the comparatively high boiling point of the tribromide, 90.5°, prevents serious loss from evaporation at this temperature. The whole system was swept out with helium before bromine was introduced into the saturating bulb. Then when the reaction tube had been filled with helium saturated with bromine it was heated to redness. As high a concentration of bromine as possible was maintained by warming the saturating bulb and connection with the reaction tube. After twelve hours operation it was evident that considerable unchanged bromine was passing through the apparatus. The process was therefore discontinued.

Besides boric acid and hydrogen bromide formed by hydrolysis, silicon tetrabromide was certainly present, possibly carbon tetrabromide. The relative boiling points of the impurities lead to the

expectation of comparatively rapid purification by fractional distillation. In fact Stock and Kuss [20] have already found that, although owing to the higher temperature at which the synthesis is effected, the tribromide is likely to be more highly contaminated with the corresponding silicon compound than the trichloride, the speed of removal by fractionation is distinctly greater.

	Bpt.
BBr_3	90.5°
HBr	−69.0°
CBr_4	190. °
$SiBr_4$	153. °

Purification by fractional distillation was then carried out as illustrated in Figure 6. After the material had been poured into bulb *A*,

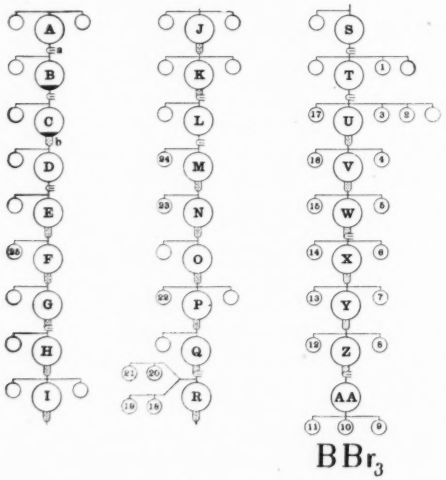

FIGURE 6.

attached to a special joint, the bulb was exhausted as far as possible by an efficient water-pump and sealed. Distillation into *B*, containing mercury, freed the material from boric acid formed by hydrolysis during the unavoidable exposure to air during the preparation. Since even vigorous shaking with the mercury failed to remove all the excess of bromine, distillation into *C*, also containing mercury, followed. In *C* the color due to free bromine completely disappeared. From

this point on distillation with fractionating columns in apparatus somewhat similar to that shown in Figure 2 was continued for twenty-four distillations. Usually the still was warmed and the receiver cooled with ice. Under these conditions the fractionating column required no cooling beyond that of the air. In the distillation from *K* to *L* the receiver was cooled with carbon dioxide refrigerant. Although Fraction 25 contained considerable silicon tetrachloride, Fraction 23, consisting of about 7.5 grams was analyzed quantitatively for silicon, and none could be discovered. More and less volatile fractions were then collected for analysis, the more volatile fractions with the use of liquid air, until finally the tribromide was completely fractionated.

The Analysis of Boron Trichloride.

After being weighed the bulb containing boron trichloride was broken under an excess of ammonia and the glass was collected and weighed. The solution was diluted to considerable volume and made acid with nitric acid, and then was precipitated with a weighed very nearly equivalent amount of pure silver. The point of exact equivalence between chloride and silver was then found with the assistance of a nephelometer.

The bulb was soaked first in cleaning solution and then for at least a day in pure water. Generally the capillary was slightly scratched with a file to facilitate breaking. Next the bulb, suspended in a platinum wire basket, was weighed under water of known temperature, and the weight of the basket under water was determined at the same time. Sometimes these operations were carried out before the cleaning. After being dried with a clean nearly lintless cloth, the bulb was allowed to remain at least over night in a desiccator containing fused potassium hydroxide. Weighing by substitution followed, and the temperature, pressure and humidity of the balance case were observed at the same time. From the loss in weight under water the volume of the bulb was computed, and then from the atmospheric conditions the buoyant effect of the air on the bulb. In the later experiments the atmospheric density was found from the weight of a sealed, standardized globe.[21]

For breaking the bulb and hydrolyzing the trichloride a 2-liter heavy walled Jena or Pyrex flask, fitted with a carefully ground glass stopper, was employed. About one hundred and twenty-five cubic centimeters of pure water were placed in the flask and ammonia, generated by boiling a concentrated solution, was introduced in slight excess of the amount necessary to neutralize the acids formed in

hydrolysis. After the bulb had been carefully lowered into the solution, the flask was stoppered and cooled with ice. With the walls of the flask wet with ammonia solution the bulb was broken by shaking the flask. No difficulty was experienced in this step in the process with the trichloride, but, as stated later, the tribromide is likely to react with explosive violence.

Although the fog produced in the decomposition disappeared within a half hour, the flask was never opened for two hours. Occasional shaking was employed to hasten the absorption of the fog. In every case, except for glass fragments, the resulting solution was perfectly clear.

The glass was now washed thoroughly by decantation and was finally collected on a filter paper, while the solution was received in a large glass-stoppered precipitating flask or bottle.

After the filter paper with the glass had been dried in a weighed platinum crucible, the paper was charred and the residue burned at the lowest possible temperature. Following a preliminary weighing the glass was fused in the crucible and the system reweighed. In nearly every case the change in weight on fusion was within the limit of error of weighing, and the average weight of glass was used in the final computations.

In order to determine the efficiency of the washing of the filter, empty glass bulbs which had been weighed open to the air were broken under a solution prepared by decomposing boron trichloride with ammonia, and the glass fragments were collected and weighed as above. Small differences between the original weight of the bulb and the final weight of the glass fragments were found as follows:

	gram
	−0.00007
	+0.00011
	+0.00025
	+0.00022
Average	+0.00013

This difference, though small, was traced to slightly faulty technique in washing, for two similar experiments where the method of washing was slightly improved, the corresponding difference was only 0.02 mg. in each case.

If the excess in weight in the earlier experiments is boric oxide, a corresponding amount of chloride must have been lost. These errors partially compensate so that with a five gram sample of material the observed atomic weight would be raised only 0.0004 unit. In the later analyses this difficulty was, of course, avoided.

From the weight of the bulb corrected for the buoyancy of the air on bulb and weights was subtracted the weight of glass, also corrected to vacuum, in order to find the correct weight of boron trichloride.

In all the analyses of Series I, after the ammoniacal solution of ammonium borate and chloride had been diluted to a volume of between one and one-half liters, it was made slightly acid by the addition of dilute nitric acid, and then, after precipitation, the acidity was increased by the addition of concentrated nitric acid to 0.1 normal concentration. In Series II and IV immediately before precipitation it was made still more strongly acid by the addition of 3 or 6 normal nitric acid through a funnel tube extending to the bottom of the solution, until in general the final solution was about normal in acidity. Since Hönigschmid [22] has found that even three normal nitric acid liberates no chloride from a similar quantity of potassium chloride the acidity was not dangerous, especially as the condition was temporary.

From the corrected weight of boron trichloride the weight of silver necessary to precipitate the chloride was computed. This quantity was weighed out, chiefly in the form of a very few large buttons, the final adjustment being made with small electrolytic crystals. After careful solution of the silver in chloride-free nitric acid, and elimination of the nitrous acid and oxides of nitrogen, in a flask provided with a spray trap in the form of a column of bulbs ground into the neck, the solution was diluted to less than tenth normal concentration and then was added slowly with constant agitation to the chloride solution. The mixture was allowed to stand for several days with occasional shaking, before testing for excess of chloride or silver in a nephelometer. If a deficiency of either was found, it was made up by adding hundredth normal solution until the end point had been reached. Even then the solutions were allowed to stand for some weeks longer with occasional shaking in order to allow included or occluded material to be extracted from the precipitate. Only slight changes were ever produced by thus standing.

In Analyses 12, 14 and 15 of Series II and in Analysis 13 of Series IV, fifty cubic centimeters additional of concentrated nitric acid were added to the silver nitrate solution before precipitation. Variations in the acidity of the solutions before and after precipitation produced no apparent effect.

The manipulation of precipitation and testing of the solutions were carried out in ruby light. In using the nephelometer all the precautions noted by Richards and Wells [23] were observed, such as preparing the comparison tubes under as nearly as possible identical con-

ditions of temperature, concentration and time, allowing the tubes to come to constant ratio by standing for an hour or more, and taking the average of several readings of each ratio.

In several analyses the weight of the silver chloride was determined. The first three experiments were completed in the usual way. In order to lower the solubility of the precipitate 0.05 gram of silver nitrate per liter of solution was added, and after vigorous shaking the analysis was allowed to stand for twenty-four hours.

Filtration of the supernatant liquid through a weighed platinum sponge crucible was followed by thorough washing of the precipitate by decantation with a solution of silver nitrate also containing 0.05 gram per liter. Pure water was used for the final washing and transference of the precipitate to the crucible. The precipitate was dried at about 260° in an electrically heated porcelain oven for sixteen hours before being weighed. Moisture retained by the precipitate was determined by fusing the main bulk and finding the loss in weight on fusion. The solubility of the silver chloride in the mother liquor and silver nitrate washings was assumed to be 0.05 mg. per liter.[24] The silver chloride dissolved in the aqueous washings together with that obtained by rinsing the precipitation flask with ammonia was estimated by nephelometric comparison with standards. The concentration of silver chloride in the aqueous washings did not vary much from 1.2 mg. per liter in the different experiments.

Since in these first three experiments the weight of silver chloride was perceptibly less than that corresponding to the silver used in the comparison, the suspicion was raised that owing to the rather high concentration of ammonium salts and nitric acid in the mother liquor the solubility of the silver chloride might be larger than the assumed value. In the next analysis (Series III, Analysis 4) no silver nitrate was added to either mother liquor or washing liquid. These solutions were combined and evaporated to dryness. The residue was dissolved and filtered and the vessel in which the evaporation occurred was rinsed with ammonia and the rinsing was poured through the filter. A small quantity of potassium iodide was added to this solution and then an excess of nitric acid. The resulting silver iodide was collected on a small platinum sponge crucible, dried and weighed. The iodide thus obtained indicates a solubility of silver chloride in the mother liquor of 2.40 mg. per liter, a value nearly twice as large as that in pure water. In the next experiment (Series III, Analysis 5) the mother liquor alone was evaporated, and by a similar treatment was found to contain 2.37 mg. per liter. This result is in accord with earlier ob-

servations of the increase in solubility of silver chloride in increasing concentrations of nitric acid.[25]

In another analysis (Series III, Analysis 6) an excess of 0.5 gram of silver nitrate was added to the mother liquor, which was then cooled with ice. The solubility under these conditions was assumed to be negligible. Ice cold water was used in rinsing the precipitate, and the dissolved silver chloride was determined by nephelometric comparison.

In the seventh analysis (Series III), no silver nitrate was added either to mother liquor or to washing liquid, but the mother liquor and washing liquid were ice cold during filtration. After evaporation the dissolved silver was determined as silver iodide. In this experiment, after the silver chloride had been fused in a quartz crucible and weighed, it was again fused, in a current of dry chlorine. A gain of 0.29 mg. resulted. A second fusion in air then caused a loss in weight of 0.02 mg. and fusion in chlorine for over four hours resulted in a loss of 0.08 mg. more. The weight after the first fusion in chlorine is used in the calculation.

The Analysis of Boron Tribromide.

The weight of boron tribromide was found in very nearly the same way as in the experiments with trichloride. Considerable difficulty was experienced in hydrolyzing the tribromide, owing to the extraordinary violence of the reaction. In four cases the pressure developed was high enough to burst the heavy walled reaction flask. This effect has already been noted by Abrahall [26] and by Gautier.[27] We were unable to determine the exact cause of the effect, nor did variations in the temperature, volume and concentration of the ammonia solution, nor substitution of pure water for ammonia (Series IV, Analyses 5 and 6) eliminate the difficulty. Furthermore the decomposition flasks were apparently weakened by use, for in several cases a flask which had been successfully used several times succumbed to the effect of a sample of tribromide smaller than some already hydrolyzed in the same flask. As soon as the danger was discovered, the breaking flask was surrounded with cloth and a stout wooden box during the decomposition, so that no untoward results occurred on those occasions when the flask burst.

The comparison of the solution of tribromide with silver was conducted as described in the case of the chloride. Freedom from chloride was indicated by the fact that at the end of the comparison with silver the mother liquor gave almost no opalescence with either silver or bromide solutions.

In Series IV, Analysis 8, the solutions were both diluted to over three liters before precipitation.

The tribromide used in Analyses 6, 7 and 13 had a slight yellow tint, possibly owing to decomposition when the capillary of the bulb was sealed with a blast flame.

In two experiments the silver bromide was collected and weighed. Owing to the lower solubility of silver bromide, the process offers fewer difficulties than that of determining silver chloride. The precipitate was washed only with pure water in the first experiment and a correction of 0.1 mg. per liter was applied to correct for solubility.[28] In the second experiment 0.02 gram of silver nitrate was added for each liter of mother liquor and after shaking and standing the latter was poured through a weighed platinum sponge crucible. Washing with a solution containing 0.01 gram silver nitrate per liter was followed by rinsing and transferring to the crucible with chilled water. No correction for solubility was applied in this experiment. Moisture retained by the bromide was determined as described in the case of the silver chloride.

Weighings were made on a No. 10 Troemner balance, sensitive to 0.02 mg. with a load of fifty grams. The beam was graduated to 0.05 milligrams, and the 5 milligram rider was used to determine all quantities larger than this, interpolation from the zero points being employed for amounts less than 0.05 milligram.

The weights were of gold plated brass, except the fractional weights, and were compared by the Richards substitution method.[29]

All weighings were by substitution. In the case of the bulb and the silver, the weights were substituted for the object weighed. In the case of the glass and the silver halides, the crucibles were substituted for similar counterpoises. A small quantity of impure radium bromide was kept in the balance case to prevent electrostatic effects.

Vacuum corrections were applied as follows:

TABLE 1.

	Density	Vacuum Correction per Gram
Weights	8.3	
Air	0.001293 at 0° and 760 mm.	
Glass	2.5	+0.000335
Ag	10.49	−0.000031
AgCl	5.56	+0.000071
AgBr	6.47	+0.000041

Humidity was read on an accurate hair hygrometer.

Results.

TABLE 2.

$BCl_3 : 3\,Ag$

Series I. Sample I.

Ag = 107.880 Cl = 35.458

Number of Analysis	Fraction of BCl_3	Weight of BCl_3 in vacuum gm.	Weight of Ag in vacuum gm.	Weight of Ag added or subtracted in solution gm.	Corrected Weight of Ag in Vacuum gm.	Ratio $BCl_3 : 3\,Ag$	Atomic Weight of Boron
1	6	4.84825	13.39534	−0.00474	13.39060	0.363063	10.804
2	4	3.80944	10.52174	−0.00225	10.51949	0.362132	10.826
3	8	5.67738	15.67705	+0.00368	15.68073	0.362060	10.803
4	5	5.28752	14.60628	−0.00250	14.60378	0.362065	10.805
5	7	2.86895	7.92386	−0.00021	7.92365	0.362074	10.808
					Average	0.362079	10.809

Series II. Sample II.

1	25	6.63574	18.32700	−0.00315	18.32385	0.362136	10.828
2	1	6.36923	17.58436	+0.00030	17.58466	0.362204	10.850
3	24	6.37226	17.59566	+0.00100	17.59666	0.362129	10.825
4	2	5.87852	16.23532	−0.00403	16.23129	0.362172	10.839
5	3	3.73634	10.31892	−0.00094	10.31798	0.362119	10.822
6	21	3.95311	10.91956	−0.00205	10.91751	0.362089	10.812
7	4	3.53556	9.76477	−0.00241	9.76236	0.362162	10.836
8	5	3.55078	9.80597	−0.00041	9.80556	0.362119	10.822
9	19	3.45120	9.53065	+0.00123	9.53188	0.362069	10.806
10	7	3.59682	9.93334	+0.00005	9.93339	0.362094	10.814
11	9	4.33672	11.97673	+0.00005	11.97678	0.362094	10.814
12	16	3.07091	8.48141	−0.00010	8.48131	0.362080	10.810
13	11	3.70594	10.23471	+0.00076	10.23547	0.362068	10.806
14	14	3.17865	8.77846	+0.00016	8.77862	0.362090	10.813
15	6	4.35457	12.02684	−0.00055	12.02629	0.362088	10.912
16	18	4.10982	11.34969	+0.00060	11.35029	0.362089	10.812
17	12	3.62520	10.01112	+0.00060	10.01172	0.362096	10.815
					Average	0.362112	10.820

TABLE 3.

SERIES III.

$BCl_3 : 3\,AgCl$

Number of Analysis	Fraction of BCl_3	Weight of BCl_3 in vacuum gm.	Weight of AgCl in vacuum gm.	Loss on Fusion gm.	Dissolved AgCl gm.	Corrected Weight of AgCl in vacuum gm.	Ratio $BCl_3 : 3\,AgCl$	Atomic Weight of Boron
1	21	3.95311	14.50419	0.00023	0.00156	14.50552	0.272525	10.816
2	5	3.55078	13.02480	0.00027	0.00168	13.02621	0.272587	10.842
3	19	3.45120	12.66314	0.00020	0.00186	12.66480	0.272503	10.806
4	16	3.07091	11.26100	0.00027	0.00746	11.26819	0.272529	10.817
5	14	3.17865	11.65561	0.00020	0.00741	11.66282	0.272546	10.825
6	7	3.59682	13.19721	0.00022	0.00090	13.19789	0.272530	10.818
7	4	3.53556	12.96603	0.00020	0.00462	12.97045	0.272586	10.842
						Average	0.272544	10.824

TABLE 4.
SERIES IV.
$BBr_3 : 3\,Ag$

Ag = 107.880 Br = 79.916

Number of Analysis	Fraction of BBr_3	Weight of BBr_3 in vacuum gm.	Weight of Ag in vacuum gm.	Weight of Ag added or subtracted in solution gm.	Corrected Weight of Ag in vacuum gm.	Ratio $BBr_3 : 3\,Ag$	Atomic Weight of Boron
1	24	11.94682	15.42985	−0.00254	15.42731	(0.774394)	(10.877)
2	22	16.70949	21.58073	+0.00200	21.58273	0.774207	10.816
3	18	10.62202	13.71837	+0.00120	13.71957	0.774224	10.822
4	20	5.72663	7.39441	+0.00230	7.39671	0.774213	10.818
5	4	8.72710	11.27176	−0.00003	11.27173	0.774247	10.829
6	3	8.01796	10.35691	−0.00178	10.35513	0.774298	10.846
7	5	7.99444	10.32534	+0.00049	10.32583	0.774218	10.820
8	6	7.05884	9.11711	−0.00049	9.11662	0.774283	10.841
9	15	10.56234	13.64286	−0.00015	13.64271	0.774211	10.818
10	14	7.92601	10.23772	−0.00046	10.23726	0.774232	10.824
11	13	9.11150	11.76854	+0.00079	11.76933	0.774173	10.805
12	8	10.45731	13.50635	+0.00020	13.50655	0.774240	10.827
13	9	9.20250	11.88626	−0.00067	11.88559	0.774257	10.833
14	10	8.85374	11.43584	+0.00071	11.43655	0.774162	10.802
15	11	4.75503	6.14174	+0.00037	6.14211	0.774169	10.804
				Average, omitting Analysis 1		0.774224	10.822

TABLE 5.
SERIES V.
$BBr_3 : 3\,AgBr$

Number of Analysis	Fraction of BBr_3	Weight of BBr_3 in vacuum gm.	Weight of AgBr in vacuum gm.	Loss on Fusion gm.	Dissolved AgBr gm.	Corrected Weight of AgBr in vacuum gm.	Ratio $BBr_3 : 3\,AgBr$	Atomic Weight of Boron
1	10	8.85374	19.90872	0.00028	0.00039	19.90883	0.444714	10.799
2	8	10.45731	23.51239	0.00020	0.00000	23.51219	0.444761	10.825
						Average	0.444738	10.812

Discussion of Results.

It has already been pointed out that the first sample of boron trichloride was made from boron suboxide which had been extracted with hydrobromic acid, and therefore may have contained a trace of tribromide, in spite of the fact that the material at first contained an excess of chlorine. The difference in the boiling points of the trichloride and tribromide is so large, however, that it seems reasonable to expect that if the tribromide was actually present as impurity in the trichloride it was eliminated in the fractional distillation together with the silicon halides. Furthermore, the effect of tribromide as impurity would be to raise the apparent atomic weight of boron, whereas the experiments of Series I give a result somewhat lower than those of the later series. In Series I also the uncertainty exists as to the washing of the filter paper in the determination of the glass, but as already pointed out on page 34 this uncertainty is scarcely large enough to affect the third decimal place in the atomic weight of boron. The earlier analyses of Series II and III are subject to the latter uncertainty, but there seems to be insufficient reason to reject analyses on this account.

The question of the ultimate elimination of silicon halides has been answered in part by direct evidence both of the progressive separation by the fractional distillation and of the absence of appreciable proportions of silicon compounds in fractions less pure than those analyzed.

The only evidence as to the complete elimination of hydrogen halides must necessarily come from the results of the analyses. In Table 6 the analyses are arranged in the order of decreasing volatility of the fractions. No systematic trend is apparent except possibly a tendency toward high results with the most volatile fractions. Since hydrogen chloride would lower, not raise the apparent atomic weight of boron the tendency can not be ascribed to this impurity. Nor can it be ascribed to silicon halides since these would be contained in the less volatile fractions. On the whole the uniformity of the material over such a wide range of fractions is satisfactory.

TABLE 6.

Series I.		Series II and III.			Series IV and V.		
Fraction	Atomic Weight	Fraction	Atomic Weight		Fraction	Atomic Weight	
4	10.826	1	10.850		3	10.846	
5	10.805	2	10.839		4	10.829	
6	10.804	3	10.822		5	10.820	
7	10.808	4	10.836	10.842	6	10.841	
8	10.803	5	10.822	10.842	8	10.827	10.825
		6	10.812		9	10.833	
		7	10.814	10.818	10	10.802	10.799
		9	10.814		11	10.804	
		11	10.806		13	10.805	
		12	10.815		14	10.824	
		14	10.813	10.825	15	10.818	
		16	10.810	10.817	18	10.822	
		18	10.812		20	10.818	
		19	10.806	10.806	22	10.816	
		21	10.812	10.816			
		24	10.825				
		25	10.828				

The most convincing evidence that both halides were ultimately pure and that no serious analytical error exists is the concordance between the results of the chloride and bromide analyses. It is difficult to believe that two substances differing so widely in physical properties both contained after fractionation proportions of impurity which produced identical effects.

Further comparison of the results may be made by grouping the experiments according to the specimen of pure silver used. This has been done in Table 7. Here again the differences are no larger than the experimental error.

TABLE 7.

Sample of Silver	Analyses	Average Atomic Weight of Boron
Scott	Series II, Analyses 5–12 Series IV, Analyses 7–14	10.818
Tani	Series I, Analyses 1–5 Series II, Analyses 1–4	10.822
Weatherill	Series IV, Analyses 1–6	10.824
Dorcas and Hilton	Series II, Analyses 13–17	10.813

The mean of the averages of Series I to V is 10.817. If each average is weighted according to the number of analyses, the mean is 10.820. This latter value is almost identical with the average of Series II and IV, the most reliable of the four. It is interesting to note that Abra-

hall [26] in his final series of analyses of boron tribromide by comparison with silver obtained a result identical with that of our analyses of the same substance. Furthermore Hönigschmid and Birckenbach believe that the value 10.82 best represents the outcome of their work. It is especially reassuring that material prepared and analyzed under such widely differing conditions should yield so concordant results as theirs and ours.

Direct confirmation of the existence of isotopes of boron was obtained by Aston [31] by the use of the mass spectrograph. These isotopes were found to have the masses 10 and 11, the latter being more abundant. Aston states, "The relative photographic intensity of the lines 5 and 5.5[32] does not agree well with an atomic weight as high as 10.9, ..." Aston later [33] estimates the mean atomic weight from the relative intensities of the mass spectrum lines to be 10.75 ± 0.07. The value 10.82 is in accord with this estimate and corresponds to relative proportions of 1 to 4.5 of the isotopes 10 and 11 respectively.

With two isotopes of boron, chlorine and bromine, there are evidently possible eight different trichlorides of boron as well as eight different tribromides, with molecular weights ranging from 115, at intervals of one unit, to 122 in the case of the chloride, and from 247 to 254 in the case of the bromide. Of these, the chloride $B^{11}(Cl^{35})_3$, 116, and $B^{11}(Br^{79})_3$, 248, are presumably the most abundant, and $B^{10}(Cl^{37})_3$, 121, and $B^{10}(Br^{81})_3$ the least abundant. The question therefore may be raised as to whether partial separation may have occurred during the fractionation of the two liquids.

As pointed out by Baxter, Weatherill and Scripture [9] in the case of the silicon halides, separation, if it occurs at all, should continue throughout the fractionation. Since no systematic difference in the composition of fractions covering a large proportion of the material is apparent, it is reasonable to conclude that no appreciable separation of isotopic substances was taking place. Furthermore perceptible separation is to be expected only during distillation at extremely low pressures, as has already been pointed out several times by others, whereas in the distillation of the boron trihalides this was far from being the case.

Experimental evidence that isotopic separation was inappreciable is furnished by the ratio between the silver used in a comparison with the boron halide and the silver halide obtained in the second step in the same analysis, for separation of the halogen isotopes is as probable as the separation of boron isotopes. The following tables give the values of the silver-halide ratios.

TABLE 8.

Series II and III.

Fraction of BCl_3	Ratio Ag : AgCl
4	0.752662
5	0.752756
7	0.752650
14	0.752701
16	0.752677
19	0.752628
21	0.752645
Average	0.752674
Richard and Wells found [34]	0.752627

Series IV and V.

Fraction of BBr_3	Ratio Ag : AgBr
10	0.574449
8	0.574446
Average	0.574448
Baxter [35] found	0.574453

The differences between the values of the chloride ratio and that found by Richards and Wells is not too great to explain by the difficulty experienced from the increased solubility of silver chloride in the mother liquors of an analysis. Certainly there is no systematic trend with continued fractionation. The bromide ratio is essentially identical with that found directly by Baxter.

In order to test the matter further several syntheses of silver chloride were made from hydrochloric acid obtained from fractionated silicon and boron halides. The silver chloride produced in the analyses of the above halides was reduced with clean zinc in slightly acid solution. After adding an excess of sulfuric acid to the resulting solution of zinc halide, the hydrochloric acid was distilled and collected and was further purified by two distillations through a quartz condenser. Very small extreme fractions were rejected. The silicon tetrachloride material was obtained in the analyses of Series IV of the work of Baxter, Weatherill and Scripture.[36] The boron trichloride material consisted of the silver chloride obtained in the analyses of Series III of this paper plus that of two analyses in which the silver chloride was not weighed. One analysis (Analysis 3) was made with ordinary redistilled hydrochloric acid.

Weighed portions of pure silver were dissolved as previously de-

TABLE 9.

Ag : AgCl

No. of Synthesis	Sample of Ag	Source of HCl	Weight of Ag in vacuum	Weight of AgCl in vacuum	Loss on Fusion	Change in Cl_2	Weight of Asbestos	Dissolved AgCl*	Corrected Weight of AgCl	Ratio Ag : AgCl
			gm.	gm.	gm.	gm.	gm.	gm.		
1	Weatherill	$SiCl_4$	9.07788	12.06067	0.00020	−0.00001	0.00006	0.00082	12.06134	0.752643
2	Weatherill	$SiCl_4$	8.74097	11.61309	0.00010	−0.00008	0.00005	0.00046	11.61342	0.752661
3		ordinary	7.89493	10.48919	0.00025	+0.00012	lost	0.00027	10.48933	0.752663
4	Dorcas	BCl_3	9.83087	13.06167	0.00031	−0.00002		0.00050	13.06184	0.752641
5	Dorcas	BCl_3	10.32779	13.72293	0.00068	+0.00004		0.00035	13.72264	0.752610

Average of Syntheses 1 and 2 ..... 0.752652
Average of Syntheses 4 and 5 ..... 0.752626

* Determined as AgI.

scribed and after dilution were precipitated with a slight excess of the hydrochloric acid solutions in question. The precipitate, after coagulation and standing for several days, was collected on a Gooch crucible with an asbestos mat in the first three analyses of Table 9. The precipitate was dried as already described (page 36) and, after being weighed, was fused in a quartz crucible and the loss due to moisture was found. A second fusion in dry chlorine followed, in order to convert occluded silver nitrate into chloride. Changes in weight in the latter process were inappreciable. Asbestos shreds in the filtrate were collected on a filter paper and determined. In the last two analyses a platinum sponge crucible was employed, after it had been shown that a solution similar to the filtrate obtained in the analyses when passed through the crucible did not alter the weight of the crucible. The filtrates and washings of each experiment were evaporated separately and the dissolved silver salt was determined as silver iodide, in the fashion previously described (page 36).

The differences between the results of these syntheses and the value to be expected for the silver-silver chloride ratio, 0.752627, is not large enough to indicate any real difference between the chlorine of the distilled halides and normal chlorine.

Summary.

The results of this investigation may be summarized as follows:

1. Improved methods for the fractional distillation in vacuum of boron halides are described.

2. The analysis of pure boron trichloride and tribromide has yielded the value 10.820 for the atomic weight of boron (Ag = 107.880).

We are very greatly indebted to the Wolcott Gibbs and Bache Funds of the National Academy of Sciences for generous assistance in providing the necessary apparatus and materials, and to the United States Navy Department for furnishing helium.

Cambridge 38, Massachusetts.

NOTES.

[1] The earlier determinations are discussed by F. W. Clarke in Memoirs of the Nat. Acad. Sci., Vol. XVI, No. 3. The Constants of Nature. Part V. A Recalculation of the Atomic Weights. 4th Ed., p. 205 (1920); by Brauner in Abegg's Handb. d. anorg. Chem., Vol. III, Pt. 1, 5, (1906); and by Smith and Van Haagen, Reference 2.

[2] Smith and Van Haagen, Carnegie Inst. Pub., No. 267 (1918).

[3] For a resumé of the subject see Abegg, Handb. anorg. Chem., III, 1, 31, (1906).

[4] Baxter and Scott, Science, N. S., **54**, 524 (1921).

[5] Hönigschmid and Birckenbach, Anales Soc. Españ. Fís. Quím., **20**, 167 (1922).

[6] Stock and Kuss, Ber. d. d. chem. Gesell., **56B**, 314 (1923).

[7] Baxter, Moore and Boylston, Proc. Am. Acad., **47**, 585 (1912); Jour. Amer. Chem. Soc., **34**, 1644 (1912); Baxter and Grover, *Ibid.*, **37**, 1029 (1915).

[8] Baxter and Parsons, Jour. Amer. Chem. Soc., **44**, 577 (1922).

[9] Baxter, *Ibid.*, **44**, 591 (1922).

[10] Baxter, Weatherill and Scripture, These Proceedings, **58**, 247 (1923).

[11] Baxter, Tani and Chapin, Jour. Amer. Chem. Soc., **43**, 1080 (1921).

[12] Baxter and Hilton, Jour. Amer. Chem. Soc., **45**, 694 (1923).

[13] Moissan, Ann. chim. phys., (7) **6**, 296 (1895).

[14] Wöhler and Deville, Ann. chim. phys., (3) **52**, 88 (1858).

[15] Stock and Priess, Ber. d. d. chem. Gesell., **47**, 3109 (1914).

[16] Stock and Kuss, ibid., **47**, 3113 (1914).

[17] Stock, Kuss and Priess, *ibid.*, **47**, 3115 (1914).

[18] Bruner and Bekier, Z. Elektrochem., **18**, 369 (1912).

[19] See especially Reference 10, p. 250.

[20] Reference 16, page 3115.

[21] Baxter, Jour. Amer. Chem. Soc., **43**, 1317 (1921).

[22] Hönigschmid, Z. Elektrochem., **26**, 403 (1920); Hönigschmid and Birckenbach Ber. d. d. chem. Gesell., **54 B**, 1873 (1921).

[23] Richards and Wells, Amer. Chem. Jour., **31**, 235 (1904); Richards, **35**, 510 (1906).

[24] Kohlrausch found the solubility product of silver chloride to be 10^{-10} at 20°, Zeit. physik. Chem., **64**, 167 (1908).

[25] Glówczyński, Koll. chem. Beihefte, **6**, 147 (1914).

[26] Abrahall, Jour. Chem. Soc., **61**, 650 (1892).

[27] Gautier, Ann. chim. phys., (7) **18**, 352 (1899).

[28] Böttger, Z. physik. Chem., **46**, 602 (1903), 0.08 mg. per liter at 20°. Kohlrausch, Ibid., **50**, 356 (1905), 0.1 mg. per liter at 21°.

[29] Richards, Jour. Amer. Chem. Soc., **22**, 144 (1900).

[31] Aston, Phil. Mag. (6) **40**, 628 (1920).

[32] Second order.

[33] Aston, "Isotopes," 1922, p. 114.

[34] Richards and Wells, Carnegie Inst. Pub. No. 28, 1905.

[35] Baxter, These Proceedings, **42**, 201 (1906).

[36] See Reference 10, page 264.